Zn Doping of GaAs Films Using Coevaporation of the Elements

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ABSTRACT

High optical quality polycrystalline thin GaAs films, in the thickness range from 1.0 to 10 μ, and degenerately doped to levels of 3×10^{19}/cc, have been grown in a reproducible manner by the coevaporation techniques. An upper limit on the deposition temperature dictated by surface quality requirements results in the consistent observation of growth in the [311] or [111] textures and crystallite size significantly smaller than film thickness. This latter fact results in the mobility being limited by grain boundary scattering, the mobility being about two orders of magnitude smaller than for equivalently doped bulk GaAs. Using Zn diffusion methods on already deposited, undoped, high resistivity GaAs films results in large particle size but discontinuities in the films. Partial epitaxy on polycrystalline GaP substrates resulted in two-order-of-magnitude improvement in resistivity. These results tend to rule out use of polycrystalline GaAs films for applications where particle size of the order of film thickness is required. Epitaxial films are mandatory for equivalent bulk mobility applications.

PROBLEM STATUS

This is a final report on one phase of the project; work on other phases is continuing.

AUTHORIZATION

Zn DOPING OF GaAs FILMS USING COEVAPORATION OF THE ELEMENTS

INTRODUCTION

In 1965 Scheer and van Laar (1) reported on improved photoemission yields from cesiated p-degenerate bulk GaAs. An energy band picture for this system is shown in Fig. 1. Briefly, the physics of this system is as follows: the bulk GaAs is p-doped to greater than 1×10^{19}/cc, forcing the Fermi level down on top of the valence band; since the forbidden band gap for GaAs is 1.38 eV, the Fermi level is approximately 1.38 eV below the conduction band; metallic cesium, whose work function is about 1.4 eV is evaporated onto the clean, ordered, GaAs surface in ultrahigh vacuum; from the principle of detailed balancing the Fermi levels of the cesium and the GaAs must line up; under the latter condition the vacuum level of the cesium lies at about the same energy as the conduction band of the GaAs, such that the electron affinity of the GaAs-Cs system goes to zero with no barrier to emission of conduction electrons into vacuum. This system is of great interest in night-vision applications for the conversion of radiation from low level light sources into electrical energy.
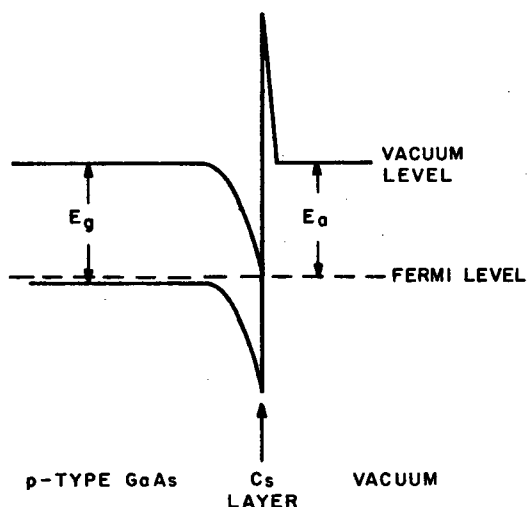

Fig. 1 – Band diagram for p-type GaAs after the deposition of Cs on the surface. E_A is the surface activation energy, and E_g is the band gap.

Since one of the major applications of this system is in devices which are illuminated from the back, that is, from the GaAs side of the system, it is required that the GaAs be in the form of thin homogeneous films. This can be seen as follows: Lambert's law describes the optical absorption of radiation in solids and is

$$I = I_0 \exp -\alpha x,$$

where I_0 is the intensity of the incident radiation, x is the distance into the solid at which the radiation I is observed, and α is the absorption constant for the material. For GaAs at the band edge, $10^3 \leq \alpha \leq 10^4$ cm^{-1}. This means that in a thickness of 1 μ the intensity is down by 1/e. As a consequence for the applications under consideration the following criteria apply to the GaAs: it must be in thin film form (0.1 to 1 μ), it must be p-doped to $> 1 \times 10^{19}$/cc, it must be optically homogeneous with a high quality front surface, it must be deposited on substrates which are transparent in the visible to near infrared, and the films should have a crystallite size the order of the film thickness. Since vacuum deposition methods seem uniquely suited to fulfill such requirements, detailed studies of the Zn-doping of vacuum-deposited GaAs films were undertaken.

## EXPERIMENTAL PROCEDURES

Evaporation System

A modified Gunther three-temperature technique, which has been previously employed in this laboratory (2), was used to deposit the Zn-doped GaAs films. This system is shown in Fig. 2. To guarantee that only the stoichiometric compound will form and remain on the substrate the following principles were used: (a) a substrate temperature is chosen such that free Ga or the compound GaAs can remain on the substrate but such that free As will have a sticking coefficient of zero; (b) the As source temperature, the Ga source temperature, and the main envelope temperature were chosen such that a surplus of As atoms arrive at the substrate for each free Ga atom arriving; and (c) where possible, sources were indirect to provide for selective impurity absorption during transfer down the tube walls to the substrate. The source configurations are shown in Fig. 2b and in more detail in Fig. 2c.

All of the source temperature zones were controlled with silicon-controlled-rectifier temperature controllers with the exception of the main envelope temperature, which used a relay actuated controller. The substrate thermocouple was mounted inside the vacuum envelope as shown in Fig. 2b. The substrate thermocouple and controller accuracy and reproducibility were periodically calibrated against a thermocouple mounted on an empty sample holder and a special flange. There was no evidence of any significant deviation in this calibration. The temperatures of the three source materials, however, were constantly monitored with one or more monitor thermocouples per oven, as shown in Fig. 2c, to check the constancy of these controllers and the individual thermocouples. This has proved necessary, as we found significant deviations between controller-indicated temperature and true source temperature. These deviations were the result of high temperature degradation of the thermocouple wire and of thermocouple misalignment. We have noted that there was a significant change in film properties with small deviations in deposition parameters. Variations in the performance of the controllers themselves were not found to be significant.

Substrate Material and Preparation

The substrates used were fused quartz, polycrystalline GaP, and mechanically polished sapphire (Al$_2$O$_3$) cut from boules supplied by Union Carbide. Quartz substrates were employed for most depositions, since they were readily available and satisfied the optical criterion of transparency in the visible. (Device use requires illumination from the substrate side of the film-substrate combination.) The sapphire used early in the program had large concentrations of work damage; however, since epitaxy was not a major requirement, this material was considered suitable for study. The GaP used was polycrystalline with large area crystallites (200 to 2000 microns on a side).
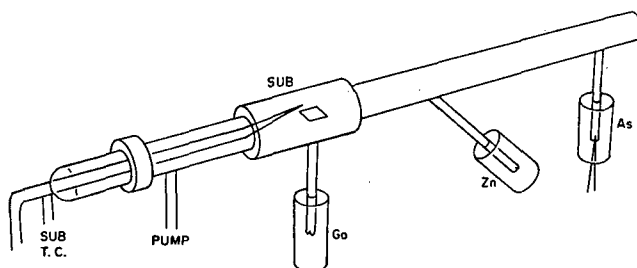
(a) Indirect Zn source
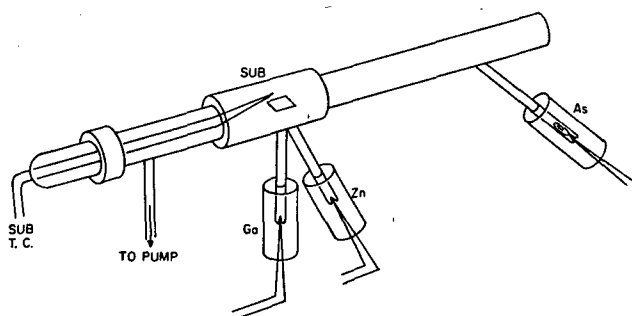
(b) Direct Zn source
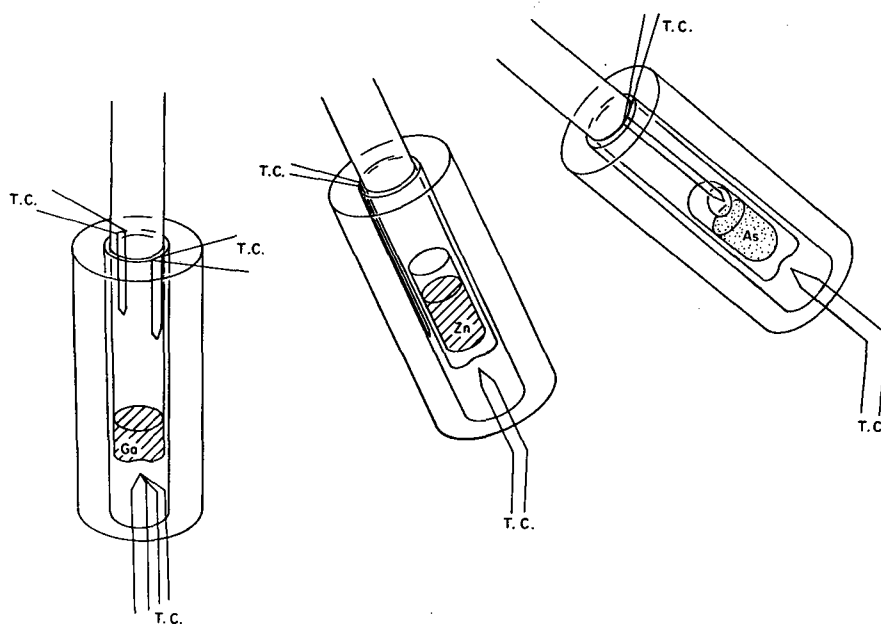
(c) Zn, As, and Ga sources and ovens

Fig. 2 – Vacuum deposition apparatus
used to grow GaAs films doped with Zn

All substrates were cleaned in hot organic solvents such as acetone, ethanol, methanol, and trichloroethelene. In the case of GaP the polished substrates were etched in a solution of 1:1 HF and H_2O_2 until the polish damage was removed, and the etching was stopped with distilled deionized water. A final cleaning in hot ethanol vapor prior to loading into the system was used on both the sapphire and GaP. The fused quartz was cleaned with a standardized glass cleaning procedure. The substrate was first heated in a saturated solution of KOH in ethanol then removed and rinsed with distilled water. This was followed by boiling in aqua regia and rinsing in five rinses of distilled water. The sample was then patted dry on clean filter paper and placed on a clean quartz holder, where it was heated with a hydrogen-oxygen torch almost to the softening point. While still hot, substrates were mounted and loaded into the vacuum system.

The substrate holder was made of Ta and etched in CP4 after every run to remove deposited material which might contaminate subsequent depositions. The samples were placed in a box whose bottom was the evaporation mask. No stress was applied to hold substrates in place, but the samples were such a close fit to the holder that movement was prevented. Sample size was nominally 1/4 by 1/2 in. or 1/4 by 3/4 in. Two samples were placed side by side in the holder, and simultaneous evaporations were made. The substrate oven was large enough such that two sets of samples could be loaded at a time. Both were held in the hot zone, but only one intercepted the evaporation beam; thus two sequential runs could be made for each pumpdown cycle.

Source Properties

As in earlier work (2) on undoped GaAs films, and as shown in Fig. 2, the Ga source was direct and the As source was indirect. The initial work with the Zn deposits also employed the direct source configuration shown in Fig. 2a. It was considered that the direct source for Zn would behave similar to that for As, since Holland (3) has published information that the sticking coefficient of Zn on clean glass, at elevated temperatures, approaches zero. According to Holland (3), Zn does not condense on a clean substrate unless the substrate is precoated with atoms of a low-vapor-pressure metal or unless the Zn vapor density is extremely high. On the basis of such information the initial Zn source was indirect. Experiment showed, however, that the sticking coefficient for Zn on Pyrex was essentially unity for temperatures up to 200°C and that little or no intermolecular scattering occurred in the main envelope of Fig. 2a. That is, for all Zn source temperatures employed up to about 400°C and for main oven temperatures up to 200°C, no Zn deposits were found except on the inner walls of the main envelope opposite the Zn source. Thereafter, the direct Zn source shown in Fig. 2b was employed.

A major technical problem encountered with the Zn source was nonreproducible evaporation rates and variable resistivities in the doped films. Experiments on the Zn source showed that small particle size and uniform packing in particulate form could not be attained. Under those conditions a continuing change in evaporation rate occurred as particles of different cross section were presented to the surface during continued evaporation. To obviate this problem, Zn particles of 99.9999% purity were melted under a forming gas ambient into the shape of a compact circular cylinder. This cylinder was cut into the shape of a right circular cylinder as shown in Fig. 2c and was subsequently cleaned in aqua regia followed by rinses in dilute nitric acid and deionized water. This source provided uniform, controllable, evaporation rates. As and Ga sources had a five-nines purity.

Deposition System Processing

As designed, the apparatus was capable of producing about 150,000 Å of GaAs in either a single deposition or a number of sequential depositions. Limiting factors were

depletion of the Zn source and the formation of ZnAs on the walls of the main envelope on either side of the substrate oven.

The deposition system was always chemically cleaned with aqua regia and CP4 etchants before each set of depositions. Approximately 15 depositions 1 micron thick could be made before it became necessary to clean the tube and replenish the source materials. The Ga and As materials were prepared and loaded as previously described (2), except that the As source was not sealed. After the As source had been exposed to air, a vacuum bake at 340°C was required to drive off oxidation products. During this 2-minute bake the other sources and the substrate were maintained at sufficiently high temperatures to avoid contamination from the As source. The As source was reusable; the Ga and Zn sources were always etched away during tube cleaning.

Film deposition procedures were as follows: (a) starting with a chemically cleaned system and sources, chemically cleaned substrates were placed in the substrate oven and the system was pumped to a pressure of 10^{-6} torr; (b) the system was baked at elevated temperatures (250°C) until the base pressure reached less than 10^{-7} torr; (c) for source outgassing the main oven temperature was set at 150°C, the Ga source at 500°C, and the Zn source at 270°C; (d) under conditions (c) the As source was brought up to 340°C for about 2 minutes with the substrate temperature at about 550 to 600°C. After these treatments the system was ready for film deposition.

A systematic series of experiments involving variations in the various source temperatures, condensation rates, and geometry was undertaken to provide uniform Zn doping under conditions which would provide optimum crystallinity and doping. The choice of substrate temperature was determined by the crystallinity criterion. Since previous (4) investigations have shown that films deposited in the [110] texture are degenerate p-type films but have small particle size, we were constrained to deposit above 400°C in the [111] or [311] texture, where undoped films exhibit extremely high resistivities but with improved crystallite size. Initial investigations were undertaken at substrate temperatures in excess of 440°C. Detailed studies on films deposited at this temperature resulted in two-order-of-magnitude variations in resistivity and wide variations in surface crystal growth, resulting in twin plane reentrant growth structures and whisker formation. Both of these growth forms caused poor surface regularity and poor optical quality. It was empirically determined that restricting the maximum substrate temperature to 400°C would eliminate almost all of these problems. The lower deposition temperature does, of course, restrict crystallite growth in the films.

Measurement Techniques

Immediately after deposition all films were examined by X-ray diffraction and reflection-electron-diffraction techniques for structural consistency and approximate particle size. A standard four-point probe (Fell Co. Ltd.) was used for preliminary resistivity measurements. Samples were checked with a thermoelectric probe to confirm conductivity type. Optical measurements, such as band edge position, free carrier absorption, reflectivity and general absorption spectra were also made routinely on these samples. After these nondestructive measurements were made, Van de Pauw (5) contacts were made to the sample, and resistivity and Hall effect measurements carried out over a temperature range from 77 to 770°K; at the latter temperature the electrical contacts began to alloy with the film with destructive changes in film characteristics.

The Van de Pauw contacts were made by evaporating gold dots onto the films at 250°C; this technique has proven to be a reliable way to make ohmic contacts to all of our GaAs films. Subsequent electrical connections were made by welding 1-mil Au wire to these dots with a Hughes parallel gap welder. While all of our contacts were ohmic,

each was checked with a Tektronix 545 curve tracer prior to making any dc measurements. To facilitate the use of both high and low temperatures without problems of moisture condensation or high temperature oxidation, the samples were sealed in an inert atmosphere of He. Figure 3 shows a typical arrangement for mounting a sample in a He ambient. The film on an insulating substrate was clamped loosely to a Ta plate which was fastened to an insulating cylinder attached to the four electrical leads mounted in the glass press. A chromel-alumel thermocouple was sealed into the press also and spot welded to the surface of the Ta mounting plate. The film geometry and the order of wire placement were maintained consistent throughout the series.
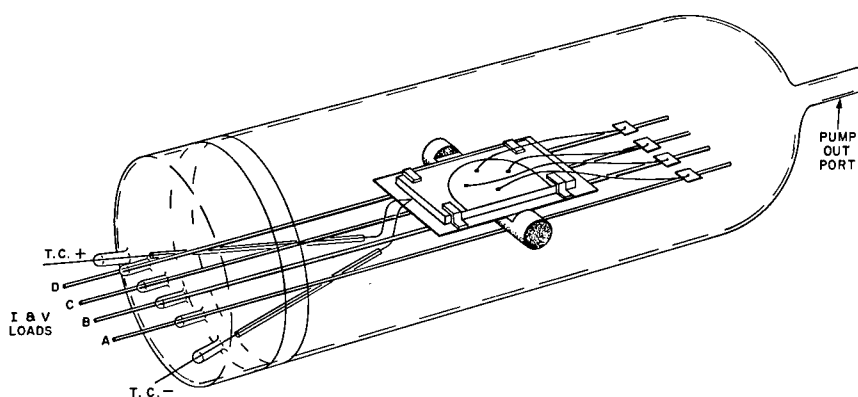

Fig. 3 – Van de Pauw resistivity and Hall measurement apparatus. The four 1-mil gold leads are attached to the evaporated contacts and to the islands on the support rods. The glass envelope used to contain the He atmosphere and the method of thermocouple attachment are shown.

EXPERIMENTAL RESULTS

Source Parameter Determination

The variations in film resistivity with Zn source temperature were measured in the temperature range from 290 to 440°C; the results are shown in Fig. 4. The points included in the upper envelope were measured on films deposited on fused quartz substrates, and the points included in the lower envelope were measured on films deposited on polycrystalline GaP substrates. The sharp rise in the resistivity at low source temperatures was the result of low Zn vapor pressures. The flattening out of the resistivity-vs-Zn-temperature curve at high temperatures was due to the solubility limit of Zn in GaAs. The films grown on the more ordered substrate, GaP, had resistivities about two orders of magnitude lower than those grown on fused quartz. This behavior is best seen for those samples where both types of substrate were used simultaneously; this is shown in Fig. 4.

The wide range of resistivity values measured for the films grown at a Zn source temperature of 350°C was the result of minor variations in the deposition conditions; small variations in the Zn source temperature resulted in significant variations in the film resistivity. The Zn source temperature of 350°C was considered optimum since it was sufficiently low to minimize appreciable loss of Zn to the external system and yet sufficiently high to allow resistivity values in the range required by device constraints. Variations in the other parameters of the system were examined, and a set of optimum
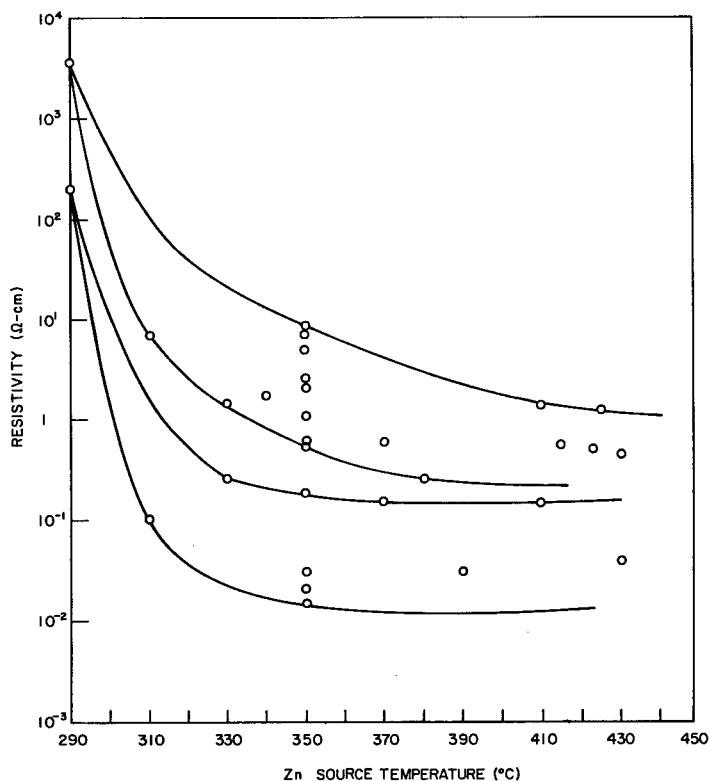

Fig. 4 – The variation of the resistivity with Zn source temperature. The upper envelope encloses data points from films deposited on SiO_2 substrates, and the lower envelope encloses data points from films deposited on GaP substrates. The 295, 310, 330, 370, and 410°C points represent simultaneous deposition on SiO_2 and GaP.

conditions were obtained for our particular geometry. These conditions are given in Table 1.

Table 1
Optimum Conditions*

Source	Source-Substrate Distance (in.)	Source Temperature (°C)
Ga	6	920 ± 2
As	Indirect	310 ± 2
Zn	6.25	350 ± 2

*Substrate temp., 400 ± 5°C; main envelope temp., 150 ± 5°C; background pressure, 10^{-6} torr.

Structural Properties

As indicated, deposition conditions constrained the examination of the properties of the films to a fairly narrow temperature range. However, two of the important device parameters were crystallite size and structure. Therefore, detailed measurements were carried out on these properties to determine device limitation. X-ray measurements were carried out on a GE-XRD-3 spectrogoniometer under high resolution conditions. Typical X-ray data for two separate films, deposited simultaneously onto different substrates, are shown in Fig. 5. The data for these degenerately doped films indicate a strong [111] texture, and the (111) reflections agree to within experimental error for the theoretical Bragg position; thus the heavy Zn doping has not caused any appreciable phase extent in the films. In general, for simultaneously deposited films on SiO_2 and polycrystalline GaP, those films on GaP were always much more highly ordered; this takes into account that the random nature of the surface crystallites in the GaP might introduce disorder. As a matter of common observation, limited epitaxy could be seen on the GaP substrates by observing the changes in reflectivity with rotation of the film under normal white light illumination. Reflection-electron-diffraction measurements supported these observations and indicated that epitaxy of GaAs on GaP could probably be easily achieved on single-crystal substrates for these deposition conditions. The lack of availability of single-crystal GaP substrates (at the time of this investigation) precluded further work in this direction.

A summary of typical X-ray data, and deviations therein, for a representative number of these films is shown in Table 2. For the substrate deposition temperature of 400°C and the inclusion of Zn the predominant textures were [111] and [311]. For the most part, reflection-electron-diffraction measurements were in agreement with the X-ray data, indicating no marked differences between crystallite growth in the bulk of the film and in the surface.

Typical reflection-electron-diffraction patterns are shown in Figs. 6a and 6b, showing the strong [111] and [311] textures. In addition an hcp film was observed, once under supposedly controlled conditions; this pattern is shown in Fig. 6c. This hcp surface growth has been previously observed by us (2) and is indicative of an excess of Ga at the substrate during the last stages of film growth. Such a condition dictates a careful examination of source properties and indicates possible deviations in either the thermocouples or controllers.

The Debye-Scherrer analysis (6) was used to determine particle size in the films using the formula

$$S = K\lambda / (\Delta^2 - \Delta_0^2)^{1/2} \cos \theta_{hkl}$$

where K is a factor determined by particle shape and ranges between 0.8 and 1.0, λ is the wavelength of the x radiation, Δ is the measured half-width of the experimental reflection, Δ_0 is the measured half-width at the instrumental broadening limit, $\cos \theta_{hkl}$ is for the particular Bragg reflection observed, and S is the crystallite size. Typical particle sizes are shown in Table 2 and range from 200 to 600 Å; these values are considerably below values required for optimum device performance.
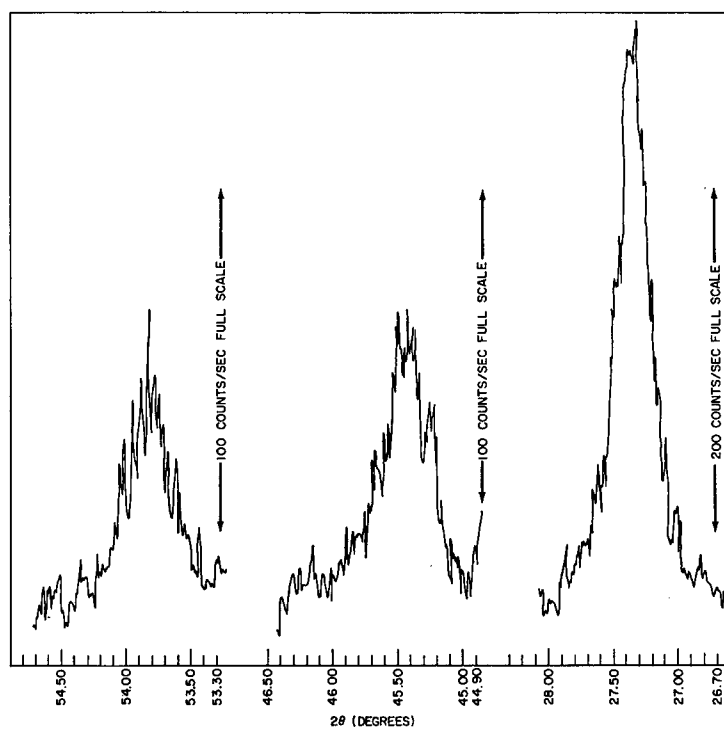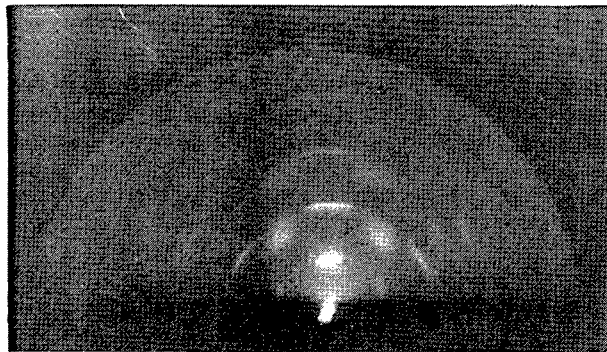
(a) D-93 on SiO_2
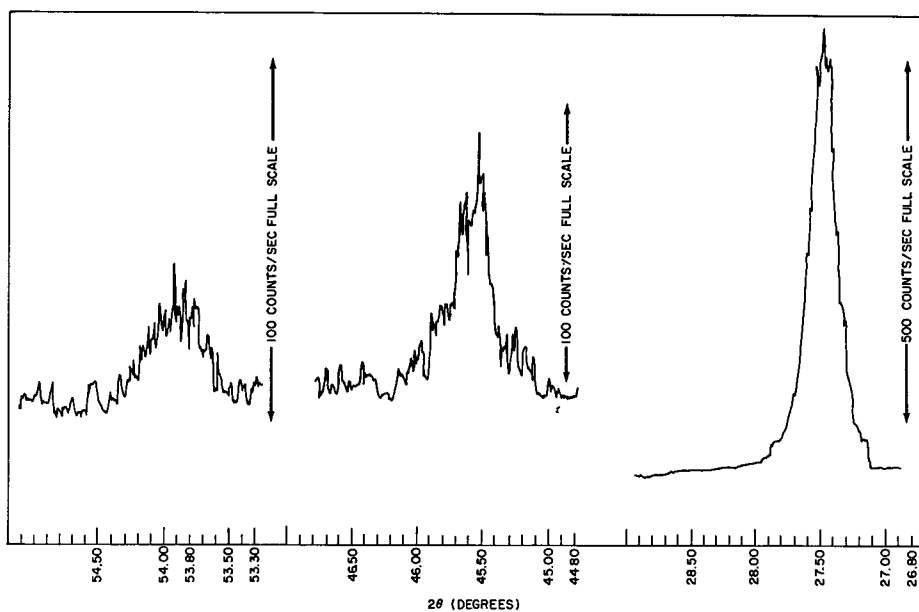
(b) D-93 on GaP

Fig. 5 – X-ray diffraction patterns for a
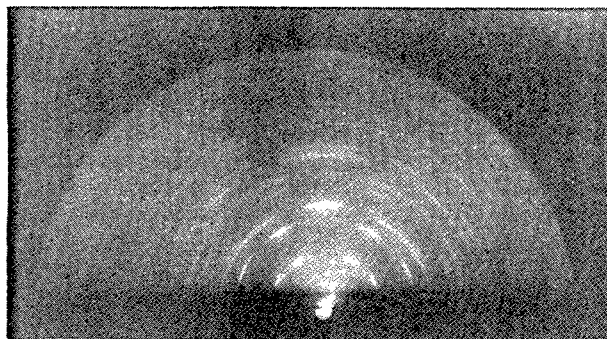pair of simultaneously deposited films

Table 2
Typical X–Ray Data

| Sample	Substrate	Conduction Type	Resistivity (ohm-cm)	Mobility	Carrier Concentration (10^{19}/cc)	Thickness (Å)	Texture X-Ray	Texture R.E.D.	Crystallite Size (Å)
D-16	SiO_2	p	84.7	—	—	6,000	—	—	—
	Al_2O_3	p	3.81	—	—	—	—	—	—
D-17	SiO_2	p	71.77	—	—	9,000	—	—	—
	Al_2O_3	p	7.47	—	—	—	—	—	—
D-18	SiO_2	p	628.0	—	—	12,000	—	—	—
	Al_2O_3	p	25	—	—	—	—	—	—
D-28	SiO_2	p	2.0	—	—	26,500	[311] [111]	[311]	200
D-29	SiO_2	p	2.0	—	—	15,000	[111] vs*	[111] vs	400
D-36	SiO_2	p	0.12	0.88	5.7	24,000	[311]	[311]	200
D-38	SiO_2	p	0.13	1.5	3	22,000	—	—	—
D-40	SiO_2	p	0.08	0.53	15	6,400	—	—	—
D-84	SiO_2	p	—	—	—	10,400	[111] vs	—	560
D-86	SiO_2	p	0.95	—	—	10,500	[111]	[311]	350
D-87	SiO_2	p	0.6	0.3	8.6	11,000	—	—	—
D-90	GaP	p	0.01	7.1	8.7	10,200	[311] [111] [311]	hcp [311]	400
	SiO_2	p	—	—	—	—			200
D-91	SiO_2	p	0.46	—	—	9,300	[311]	—	235
	GaP	p	0.026	—	—	—	—	—	—
D-93	SiO_2	p	1.16	—	—	9,600	[111]	—	350
	GaP	p	0.014	—	—	—	[111] vs	—	560
D-94	SiO_2	p	1.4	—	—	10,400	[311] vs	—	235
	GaP	p	0.20	—	—	10,400	[111] vs	—	350
D-95	SiO_2	p	4.9	—	—	10,000	—	—	—
	GaP	p	0.082	1.52	5	10,000	—	—	—
D-97	SiO_2	p	1.7	—	—	9,000	[311]	—	315
	GaP	p	0.18	—	—	9,000	[111]	—	400
D-98	SiO_2	p	0.8	0.44	1.8	9,000	—	—	—
	GaP	p	0.03	Unstable Hall voltages		9,000	—	—	—
D-99	SiO_2	p	0.088	0.7	10	10,500	—	—	—
	GaP	p	0.011	—	—	10,500	—	—	—
D-103	SiO_2	p	0.49	—	—	9,000	[111] vvs	—	400
D-105	SiO_2	p	8.5	—	—	101,600	[311] vs	—	520
D-106	SiO_2	p	0.14	1.6	7.8	106,600	[110] [111]	—	—
D-117	SiO_2	p	—	—	—	91,000	—	—	—
	GaP	p	—	—	—	91,000	—	[311]	—
D-118	SiO_2	p	—	—	—	6,000	[111] weak	—	400

*Very strong.

(a) [111] texture

(b) [311] texture
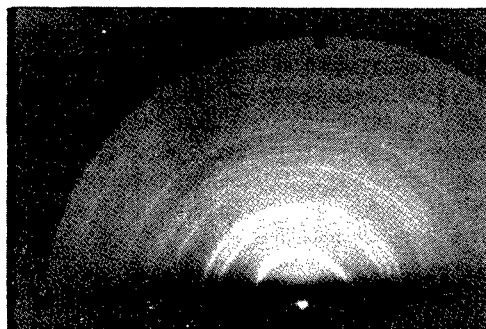
(c) Pure hcp pattern

Fig. 6 – Typical reflection–electron–diffraction plates

Electrical Properties

Table 2 shows the results of room-temperature resistivity, Hall measurements, and thermoelectric power measurements. Samples were uniformally p-type as measured by thermoelectric power measurement. Hall measurements were carried out on a large number of samples; however, extremely small Hall voltages (1-μV level) were generated in these films at magnetic fields up to 0.6 W/m^2. In addition, sample current had to be limited to values which would not cause appreciable heating in the contacts. Much of the difficulty centered in obtaining stable current and voltage sources to allow measurements at these low levels. Without nearly perfect alignment of the Van de Pauw probes the mis-alignment voltages were found to be as much as a few volts for high source currents. This then requires high-voltage-bucking circuits to be stable to less than 1 μV. These extreme conditions made Hall measurements quite difficult and in some instances impossible. However, representative data are given in Table 2. The values of the carrier concentrations were such that all of the samples were degenerate. The calculated mobilities were about two orders of magnitude lower than predicted by Sze and Irvin (7) for similar carrier concentrations. The average mobility in our films was about 1 cm^2/V-sec, whereas the extrapolated value from Sze and Irvin for equivalently doped bulk was 75 to 100 cm^2/V-sec.

Using these mobilities and calculating the mean free path (8) it was found that the value resulting from the use of the 1-cm^2/V-sec mobility was approximately equal to the average particle size (300 Å) in the films. The use of the predicted 100 cm^2/V-sec mobility, for bulk at this doping level, results in a mean free path that is two orders of magnitude larger. This is interpreted as indicating that scattering at grain boundaries limits the mobility in these films. A comparison of the resistivity data for samples where there were two different substrate materials showed that the more ordered substrate always resulted in films of lower resistivity. This was true for early work with mechanically polished Al$_2$O$_3$ substrates as well as for the GaP substrates. Since the carrier concentration is expected to be the same on two films grown simultaneously, this difference is an indirect measurement of the mobility and therefore the effects of crystallite size in the substrate and films.

Detailed measurements of resistivity vs temperature were taken in the temperature range from 77 to 700°K in the Van de Pauw geometry and the tube structure shown in Fig. 3; typical data are shown in Fig. 7. Included in Fig. 7 are data for: (a) six Zn-doped films as deposited in this work, (b) two samples prepared by vapor phase epitaxy at the Night Vision Laboratory, Ft. Belvoir, (c) a bulk single-crystal GaAs sample Zn doped to 3×10^{19}/cc, and (d) two bulk single-crystal GaAs samples Zn doped to 10^{17}/cc. The data for (d) were taken from Meyerhofer (9) and were expanded from a small portion of his published data. As cited, the lower limit of our temperature measurement was due to experimental configuration limits, and the upper limit was determined by alloying effects on the bulk GaAs samples; that is, the ohmic Au contact changed color and alloyed with the GaAs.

The shapes of these resistivity-vs-temperature curves, with the exception of the 3×10^{19}/cc bulk sample, were very similar, as expected. Our films, as well as the two Ft. Belvoir samples, exhibited what appeared to be intrinsic conduction at temperatures in excess of 500°K. Previous workers (10a) have indicated that this behavior should not occur until 900°K. The more characteristic behavior of the bulk sample, whose increase in resistivity was attributed to acoustical scattering, was present in the two films deposited on GaP. Both displayed a slight rise in resistivity prior to the onset of intrinsic conduction.

The resistivity-vs-temperature data have been analyzed according to a simple one-acceptor model according to which the slope of the ln ρ vs 1/T plot should yield E/2.
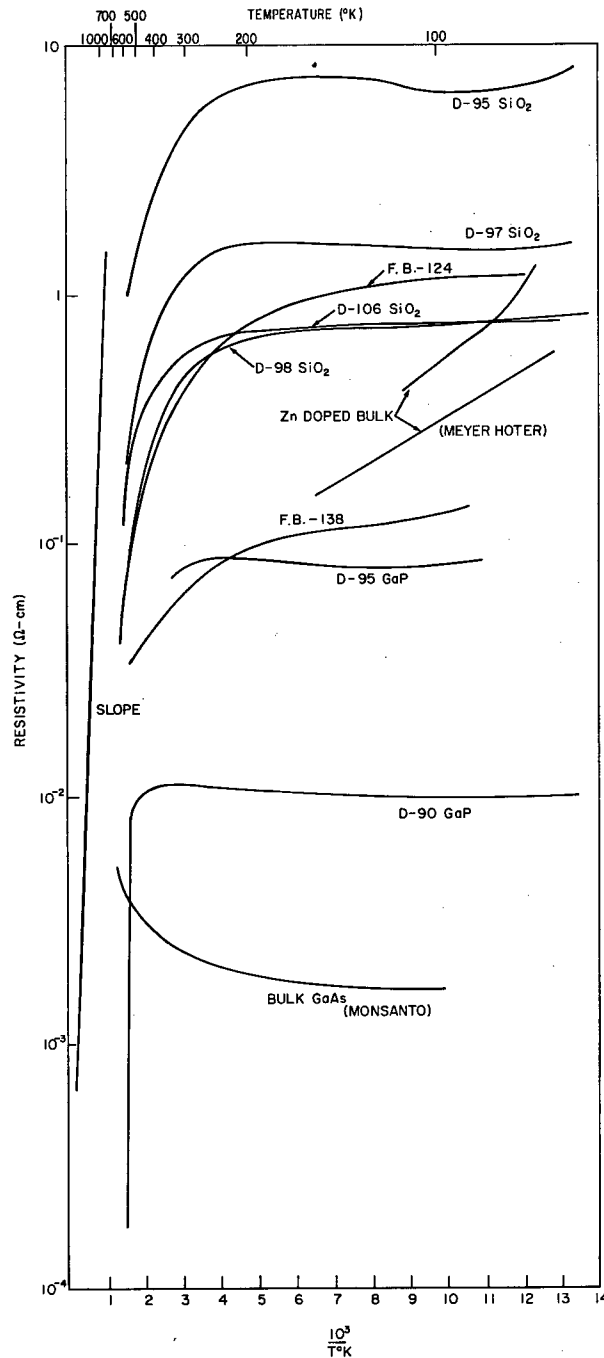
Fig. 7 – Resistivity vs temperature for films D-95, D-97, D-98, and D-106 grown on SiO$_2$, for D-95, D-90 grown on GaP, for Ft. Belvoir (F.B.) films 124 and 138, for one bulk sample of single crystal GaAs Zn doped to 10^{19}/cc, and for data from Meyerhofer (9)

In the case of extrinsic conduction, E represents the energy level of the acceptor level above the valence band. In the case of intrinsic conduction, E represents the forbidden band gap. In Fig. 7 the correspondence between the line drawn for the theoretical band gap of 1.38 eV and the slopes of the experimental data for temperatures above that temperature indicates that conduction is intrinsic above that temperature.

In principal the activation energy of the Zn impurity level can be easily determined from the one-acceptor model, but the temperature dependence of the mobility must be accounted for, and the temperature region used must be one where the level is not completely ionized. Other workers have generally used temperatures in the $50°K$ to $5°K$ range for these measurements (10b). The two curves after Meyerhofer (9) in Fig. 7 were taken from the high temperature region of his data and not from the region used for impurity level evaluation and are presented for comparison only.

The depression in the D-95 and D-97 curves in Fig. 7 at $T = 100°K$ was found at the same temperature as the maximum in the mobility reported by Hilsum and Rose-Innes (10b). Here also the effect was more pronounced at lower impurity concentrations. The radius of curvature for the transition between the extrinsic region for resistivity at temperatures below room temperature and the intrinsic region above room temperature is different for the three classes of material. Our films deposited on GaP have the sharpest transition (smallest radius of curvature), with those grown on SiO_2 being intermediate and the two Ft. Belvoir samples exhibiting the largest transition region. The relative values of the resistivity for the films grown on GaP substrates are two orders of magnitude lower than those for the films grown on SiO_2, and the Ft. Belvoir films deposited on Al_2O_3 exhibit intermediate values. For our films the more ordered films, on the GaP substrates, always have lower resistivities than those of the less ordered ones grown on SiO_2. A comparison with the Ft. Belvoir samples is qualitative only, since the matte irregular surface of the latter samples prevented accurate determination of film thickness, and typical thickness were assumed.

Optical Properties

Optical measurements on these films were in essential agreement with behavior observed for undoped films. That is, the position of the optical absorption edge is in essential agreement with that for bulk material, and the reflectivity data are in agreement with the best data on high quality surfaces. From an applications point of view these films provide surface properties of superior quality as compared with comparable vapor-phase-grown films.

Zn Doping by Diffusion

Early in the work a parallel effort was carried out using as-deposited, high resistivity, GaAs films of high quality and doping by indiffusion from an evaporated Zn surface layer. The Zn surface layer was prepared by flash-evaporating metallic Zn onto high resistivity films and subsequently heating them in a sealed tube containing sufficient As metal to provide the appropriate overpressure of As at the $670°C$ diffusion temperatures.

Initial results were quite promising. Particle sizes increased to the point where the X-ray diffraction analysis became equipment limited, indicating particle sizes of the order of film thickness. There was no evidence of stoichiometric deviation in the films. The formation of a matte surface both on the outer surface and at the quartz-film interface indicated that the Zn diffusion penetrated the film entirely.

It was not possible to make optical free-carrier absorption measurements on these films due to interference effects. Since free carrier measurements could not be made, only electrical measurements were used to characterize the films. Electrical measurements on a few typical films indicated that the films were not completely continuous. The recrystallization effects associated with the increase in particle size resulted in the growth of discrete particles over much of the film. While calculations showed the films to be degenerately doped, the disadvantage of discontinuous films did not mitigate for further work in this area.

CONCLUSIONS

It has been shown that it is possible to grow high-optical-quality thin GaAs films (0.1 to 1 μ) degenerately doped to levels of approximately 3×10^{19}/cc in a reproducible manner by the techniques described. Although the films are consistently ordered in either the [311] or [111] textures, the crystallite size is sufficiently small to limit the mean free path of charge carriers. This fact constrains the mobility to values considerably less than would be associated for bulk samples of equivalent doping. Particle-size-limited mobility is responsible for the problems associated with definitive Hall measurements. While Zn diffusion experiments indicate a solution to the small crystallite problem, the creation of discontinuous arrays of particles is not a mitigating factor for employment of the technique.

Limited epitaxy on polycrystalline GaP substrates has been observed under conditions of simultaneous deposition on Al_2O_3 and SiO_2; films on the latter substrates showed only small particle size. This observation indicates that, with proper surface treatment, and with the employment of the correct (transparent) single-crystal substrates, the particle size limitation could be overcome. In fact previous work, in this laboratory and also by Arthur (11), indicates that high quality epitaxial films are attainable using the vacuum deposition process. It is suggested that such studies could supply the requirements of the Night Vision Laboratory. Specifically the GaAs on GaP system shows great promise.

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13. ABSTRACT

High optical quality polycrystalline thin GaAs films, in the thickness range from 1.0 to 10 μ, and degenerately doped to levels of 3×10^{19}/cc, have been grown in a reproducible manner by the coevaporation techniques. An upper limit on the deposition temperature dictated by surface quality requirements results in the consistent observation of growth in the [311] or [111] textures and crystallite size significantly smaller than film thickness. This latter fact results in the mobility being limited by grain boundary scattering, the mobility being about two orders of magnitude smaller than for equivalently doped bulk GaAs. Using Zn diffusion methods on already deposited, undoped, high resistivity GaAs films results in large particle size but discontinuities in the films. Partial epitaxy on polycrystalline GaP substrates resulted in two-order-of-magnitude improvement in resistivity. These results tend to rule out use of polycrystalline GaAs films for applications where particle size of the order of film thickness is required. Epitaxial films are mandatory for equivalent bulk mobility applications.

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Additives						
Zinc						
Zinc doping						
Electrical transport properties						
Carrier mobility						
Electrical resistivity						
Hall effect						
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Crystal structure						
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